Supporting Information


Figure SI1: Decay associated differential spectra (DADS) of AO-R in MeCN







Z4



Figure SI1. Optimized structures of the 4 entgegen and the 4 zusammen conformers of AO-R obtained by quantum chemical calculations.


Figure SI2. Cyclized conformation of AO-R obtained by quantum chemical calculations.

Table SI1. Relative energy levels in $\mathrm{cm}^{-1}$ (reference is the ground state of E1) of the ground and excited states of the 8 conformers of AO-R.

| E1/E1* | $0 / 19629.4$ |
| :---: | :---: |
| E2/E2 $^{*}$ | $543.2 / 20308.8$ |
| E2anti/E2anti $^{*}$ | $670.8 / 21176.6$ |
| E1anti/E1anti* $^{*}$ | $1186.6 / 21752.8$ |
| Z1/Z1 $^{*}$ | $3048.6 / 23414.3$ |
| Z2/Z2 $^{*}$ | $4252.4 / 23772.2$ |
| Z4/Z4 $^{*}$ | $4885.3 / 24496.2$ |
| Z3/Z3 $^{*}$ | $5714.4 / 25212.9$ |

